INFLUENCE OF CRYSTALLINITY ON GAS BARRIER AND MECHANICAL PROPERTIES OF PLA FOOD PACKAGING FILMS

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ABSTRACT: Crystallinity is well-known to have major effects on the gas barrier properties. However, its effect on gas barrier properties is often dependant on the studied material and is difficult to anticipate because two aspects of crystallinity have to be considered: the crystallinity degree and the crystalline morphology.
PLA is known to recrystallize when heated at a temperature higher than its Tg ("cold" recrystalllisation). Different recrystallized samples have been obtained by compression-molding the extruded films in different conditions of heating. The crystallinity degree and morphology have been investigated and related to the gas barrier properties of the films. Since crystallinity also affects mechanical properties, the yield strength and the elongation at break have been measured.

KEYWORDS: Poly(lactic acid), crystallinity, gas permeability, mechanical properties

1 INTRODUCTION

Driven by environmental concerns, new polymers based on renewable resources are arriving on the market to replace conventional polymers, obtained from petroleum, on different applications like food packaging. One of the most prominent polymers among these materials is poly(lactic acid) (PLA), a biodegradable, thermoplastic, aliphatic polyester derived from renewable resources, such as corn starch (in the U.S.A.) or sugarcanes (in the rest of the world). Two forms are available, the PLLA that is the homopolymer and the PDLA that contains D-lactic acid and is cheaper than PLLA. These polymers present different disadvantages like low barrier properties and low mechanical properties [1].
In order to increase the gas barrier properties of polymeric materials, different solutions can be used like increasing crystallinity, multilayer coextrusion, barrier surface film coating and plasma deposition. The simplest and cheapest solution consists in increasing the crystallinity but nowadays the effects are still under consideration for PLA extruded films. Even if several studies have been conducted on this topic [2],[3],[4], most of them have been made on solvent cast films but not on extruded films. Besides, the differences between PLLA and PDLA films are usually not clearly noticed. Our previous work on PLLA films [5] showed that, surprisingly, oxygen permeability was not influenced by the increase of crystallinity. However, in this previous work, only low crystallinity degrees have been then investigated (around 37%). The objective of the present work is to determine the influence of the crystallinity on the oxygen and helium permeability of PLLA (for high crystallinity degree) and of PDLA films. Since crystallinity can also affect the mechanical properties, they are also simultaneously measured on recrystallised extruded films. Permeability and mechanical properties are finally linked with the crystalline morphology of the different films.

2 MATERIALS

The virgin materials are commercial grades. Two materials were studied : the PLLA Biomer L9000 (Biomer, Germany), being mainly in L-conformation and containing approximately 1% D-lactic acid and the PDLA NatureWorks 2002D that has a content of 2% of D-Lactic acid.

2.1 SAMPLE PREPARATION

2.1.1 Drying

Prior to extrusion processing step, both PLA were dried in an oven at 80°C during 8 hours to remove absorbed water.

2.1.2 Extruded films

The extruded PLLA and PDLA films were prepared from the dried pellets by extrusion with the conditions mentioned in Table 1. The produced films were of respectively 160 mm width and approximately 300 µm thickness. The roll temperature was set to 25°C.

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Equipment	Details
Extruder	30 mm diameter, 33 L/D length
Screw	3 zones
Mixers	4 Sulzer SMX®
Flat die	200 mm width
Extrusion conditions	
Extrusion temperature	200°C
Screw speed	40 rpm
Chill roll temperature	25°C

Table 1: *Equipment used and extrusion conditions*

2.1.3 Recrystallisation

In this study, the 160 mm width extruded films were subsequently reheated and molded at different temperatures and durations (Table 2) under compression (20 or 50 bar), to obtain PLLA and PDLA films with various degrees of crystallinity, using a thermal press (DARRAGON). They were then quenched in water in order to fix their crystallinity. These films will be named recrystallized extruded PLLA and PDLA. Sample thickness measured with a micrometer was about 300 ± 30 µm.

2.2 SAMPLE CHARACTERIZATION

2.2.1 Helium and oxygen permeability

The Helium permeability was measured at room temperature and 0 % RH using a home-made apparatus. Measurements were systematically duplicated. The oxygen permeability was also measured at 23 °C and 0% RH using a Systech 8001 (France) apparatus. Oxygen permeability is calculated from the measured oxygen transmission rate (OTR) by multiplying it by the sample thickness. Measurements were systematically duplicated.

2.2.2 Tensile tests

Tensile properties were measured using an universal tensile machine (Instron model 4507) with dumble samples cutted in the films. The yield stress and elongation at break were characterized at a cross-head speed of 5 mm/min at room temperature and humidity.

2.2.3 Crystalline morphology

The crystalline morphology of the recrystallized extruded films was observed using an optical transmission microscope NACHET, with polarized light.

2.2.4 Crystallinity degree measurement

The crystallinity degree of the films were evaluated by DSC tests (melting enthalpy of a 100% crystalline PLA = 93 J/g, [3]), performed at 10°C/min from 0 to 200°C with a Pyris 1 Perkin Elmer DSC. DSC model study was also performed: it consisted in heating the sample at the chosen recrystallisation temperature, keeping it during the recrystallisation duration and then, after cooling, in measuring its crystallinity during an additional heating.

3 RESULTS AND DISCUSSION

3.1 DSC model study and choice of the recrystallisation conditions

PLA is known to recrystallize when heated at a temperature higher than its T_g (65°C) ("cold" recrystallization) and crystallinity can be varied by modifying recrystallisation temperature and duration [3]. A preliminary DSC model study has been performed on PLLA and PDLA extruded films in order to evaluate the influence of the recrystallisation conditions on the crystallinity. Figure 1 shows that for PLLA films, crystallinity degree increases continuously with the temperature up to 60-70% for 140°C, whereas for PDLA films, this crystallinity degree remains constant around 37% until 120°C. Higher crystallinity degrees are naturally reached for PLLA because PDLA contains D forms that act as defects and so limit the crystallinity. Duration (30 min versus 90 min) seems to have little effect on the crystallinity degree for PLLA and PDLA until 130°C. Above this temperature, the recrystallisation of PDLA during 30 min leads to a crystallinity degree lower than for 90 min. It can denote a lower crystallinity rate when recrystallisation of PDLA occurs at higher temperature.

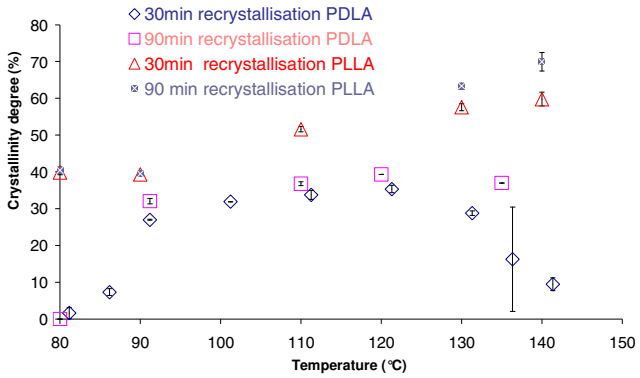

Figure 1: *DSC model study: crystallinity degree of PLLA and PDLA as a function of recrystallisation temperature and duration (30 min and 90 min)*

From this model study, the recrystallisation conditions presented Table 2 have been chosen in order to obtain films with different crystallinity degrees.

Material	Temperature (°C)	Time (min)	Crystallinity (%)
PLLA			2,5
90°C/30 min	90	30	36
120°C/30 min	120	30	54
140°C/30 min	140	30	58
PDLA			2
90°C/30 min	90	30	31
120°C/30 min	120	30	35
135°C/90 min	135	90	37

Table 2: *Recrystallisation conditions and crystallinity degrees*

3.2 Crystallinity degrees of recrystallised extruded films

Crystallinity degrees have been measured on the thermocompressed recrystallised films in order to compare them with those obtained with the DSC model study.

Crystallinity degree (%)	DSC model study	Recrystallised films
PLLA	2,5	
90°C/30 min	36	40
120°C/30 min	54	53.9
140°C/30 min	58	60.9
PDLA	2	
90°C/30 min	31	15
120°C/30 min	35	37
135°C/90 min	37	39.8

Table 3: *Comparison of the crystallinity degrees obtained by DSC model study and by film forming*

Table 3 shows a relatively good agreement, except for the "90°C/30 min" recrystallised PDLA films. This difference could be explained by the fact that at 90°C, the recrystallisation is very dependant of the duration as we can see figure 1. So a slight variation of the temperature in the recrystallisation process could easily induce a difference of crystallinity degree.

3.3 Gas barrier properties of PLLA and DLPLA

3.3.1 Helium permeability

Helium permeability of PLLA films has a particular behaviour as we can see figure 2. First, the helium permeability remains constant as the crystallinity degree increases, up to 40%. We observe then a drastic decrease of the helium permeability, with a reduction by a factor 2 when the crystallinity degree reaches 60%.

For PDLA, we observe a classical decrease of the permeability with the increase of the crystallinity degree. It is to notice that PDLA films reach the optimal permeability value ($0{,}7 m^3.m/m^2.s.Pa$) for a crystallinity degree (35%) lower than for PLLA (55%).

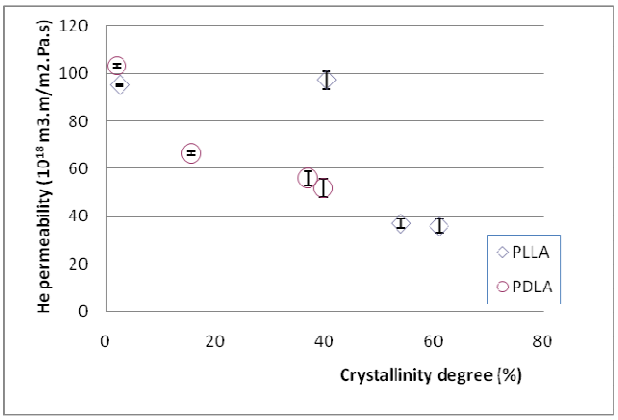

Figure 2: *Helium permeability of PLLA and PDLA films as a function of crystallinity*

3.3.2 Oxygen permeability

The oxygen permeability versus crystallinity degree of both PLAs are shown figure 3. The variation of the oxygen permeability is quite similar to the helium permeability one. Still, we can notice that the reduction of the permeability is about a factor two for oxygen, whereas it is about three for helium.

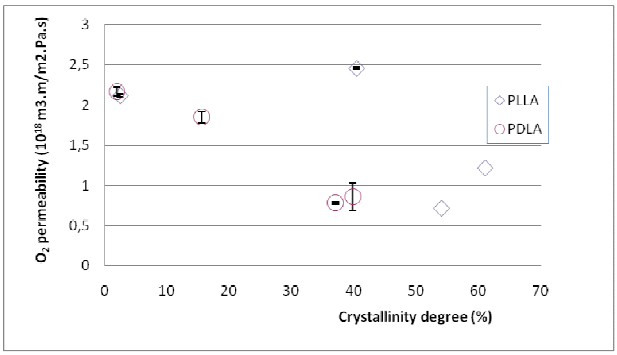

Figure 3: *Oxygen permeability of PLLA and PDLA films as a function of crystallinity*

3.4 Mechanical properties

3.4.1 PLLA films

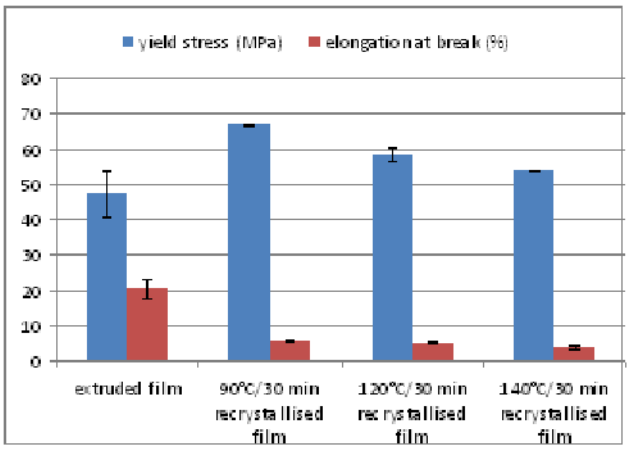

Figure 4: *Yield strength and elongation at break of PLLA extruded and recrystallised films*

Figure 4 shows that PLLA amorphous extruded films present a yield strength of around 48 MPa and a deformation at break of around 20%, that are higher than those of PS and lower than those of PET.

The recrystallisation procedure leads to an increase of the yield strength of 10 to 40%, simultaneously with a dramatic decrease of the elongation at break, that decreases to around 4% when the extruded films are recrystallised whatever the recrystallisation conditions. Moreover we can notice that the yield strength value, given for the 140°C/30 min recrystallisation films, is not obtained at the yield but at the break because of the high brittleness of this film for this condition.

3.4.2 PDLA films

As for PLLA, we see an increase of the yield strength and a decrease of the elongation at break that is still less important for PDLA than for PLLA. In particular, the samples did not become brittle and the elongation at break stayed at a higher value around 6%. This could be explained by the lower crystallinity degrees obtained for PDLA.

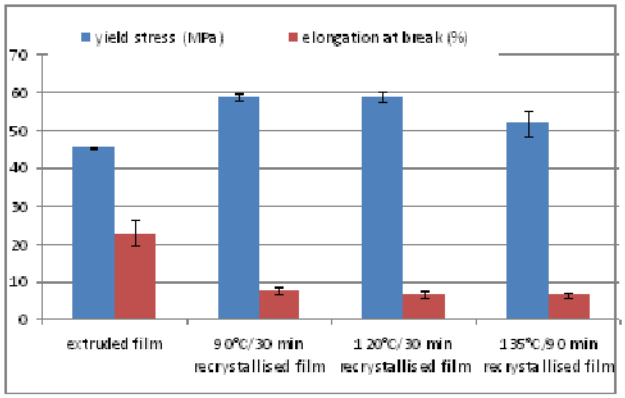

Figure 5: *Yield strength and elongation at break of PDLA extruded and recrystallised films*

3.5 Crystalline morphology

As gas barrier and mechanical properties of films are generally linked with their crystalline morphology, this last has been investigated. For all recrystallised PLLA and PDLA films, classical spherulitic domains have been observed.

For PLLA, the spherulitic domain size diameter is not modified by the recrystallisation process (around 10 micrometers). It can be deduced that gas barrier and mechanical properties are the consequence of the single crystallinity degree.

Recrystallisation conditions	Spherulitic domain diameter (µm)
90°C/30 min	5.8 +/- 1.2
120°C/30 min	14.6 +/- 1.9
135°C/90 min	9.3 +/-0.8

Table 4: *Diameter of the spherulitic domains of PDLA recrystallised films*

For PDLA, the spherulitic domain size seems to be dependant of the recrystallisation conditions, as can be seen table 4. When temperature was increased, we observed first an increase of the spherulitic domain diameter followed by a decrease when temperature is higher than 120°C. It is thus difficult to correlate these results with helium or oxygen permeability variation shown Figures 2 and 3. Nevertheless it can be correlated with mechanical properties that present maximum or minimum for 120°C. So, for PDLA recrystallised films, barrier properties seem to be affected only by crystallinity degree, while crystalline morphology could explain the evolution of mechanical properties versus recrystallisation conditions.

4 CONCLUSIONS

This study shows that PLLA and PDLA present different behaviours when recrystallised. About gas permeabilities, a singular behaviour was observed with PLLA films: it was interesting to notice that the classical decrease of the oxygen or helium permeability with the increase of crystallinity (observed for PDLA films) did not occur for crystallinity degree lower than 35%, for the recrystallisation time duration we have used in this study. Concerning the mechanical properties, recrystallisation leads to an important decrease of the elongation at break of PDLA, while PLLA films become too brittle when recrystallised. In conclusion, if single recrystallisation enhances significantly gas barrier properties of extruded PLLA and PDLA films, recrystallised PLA films needs mechanical reinforcement.

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